

**DESCRIPTION****METHOD FOR ACTIVATING SURFACE OF METAL MEMBER****Technical Field**

[0001] The invention of the present application relates to a method for the pretreatment of a metal member to activate a surface of the metal member before applying diffusion treatment such as nitriding or carburizing to the metal member.

**Background Art**

[0002] To improve mechanical properties such as abrasion resistance and fatigue strength, gas nitriding or gas carburizing that forms a nitrided layer or carburized layer in a surface of a metal member is widely applied primarily to members made of iron-based material.

[0003] Upon applying such treatment to a surface of a member made of alloy steel, especially high-alloy steel, the penetration and diffusion of nitrogen or carbon into the surface of the metal member is prevented by a passivated film (an oxide or the like) which exists on the surface of the member, thereby possibly resulting in the occurrence of poor treatment or uneven treatment of the member as a problem. Before such diffusion treatment, activation treatment is hence applied to the surfaces of metal members.

It is methods making use of chloride compounds, led by Malcomizing, that are most widely adopted as such surface activation treatment. As the chloride compounds, vinyl chloride resin, ammonium chloride, methylene chloride and the like are used.

[0004] Such a chloride is placed together with a metal member in a treatment furnace and is heated there. By this heating, the chloride is decomposed to form HCl, and the thus-formed HCl decomposes a passivated film on a surface of the metal member to activate the surface so that diffusion treatment such as nitriding or carburizing as a next step is assured.

[0005] However, the surface activation of a metal member by such a chloride results in the erosion of a furnace wall made of bricks or a metal by HCl formed through decomposition, and in gas nitriding or gas softnitriding, HCl so formed reacts with ammonia as atmosphere gas to form ammonium chloride, which not only deposits in the furnace or an exhaust system to cause troubles but also remains on the surface of the metal member (work) to induce reductions in the corrosion resistance and fatigue strength of the member.

[0006] As a substitute method for the above-described methods making use of chlorides, an activation method of the surface of a metal member with a compound of fluorine which belongs to the same halogen group, NF<sub>3</sub>, has been put into practical use in recent years (for example, Patent Document 1). Upon heating, NF<sub>3</sub> is decomposed to form fluorine, and the

thus-formed fluorine converts a passivated film on the surface of the metal member into a fluoride film to activate the surface of the metal member. The activation method of the surface of the metal member with the fluorine compound ( $NF_3$ ), however, requires sophisticated treatment for the detoxification of  $NF_3$  and HF contained in effluent gas, which prevents the wide-spread adoption of the method.

[0007] The above-described activation methods for the surfaces of metal members, which make use of halides, respectively, involves problems such as troublesome furnace deposits, furnace wall erosion and the need for detoxification treatment facilities for effluent gas. From the foregoing background, developments of activation methods for the surfaces of metal members, said methods making use of no halide, are under way.

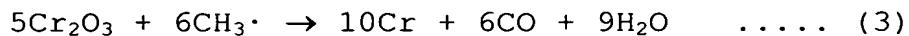
[0008] The ammonia gas nitriding method disclosed in Patent Document 2 reductively activates a passivated film on a surface of a high-chromium alloy steel member by forming reducing radicals and CO at the surface of the alloy steel member through the pyrolysis of acetone. According to this method, acetone is pyrolyzed on the heated surface of the high-chromium alloy steel member in accordance with the below-described formula (1) so that reducing radicals and CO are formed at the surface of the high-chromium alloy steel member.



An oxide film (MO) on the surface of the metal member is reduced in accordance with the following formula (2):



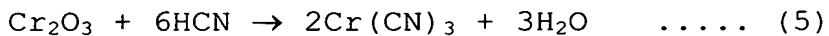
As the principal component of the surface oxide film of the high-chromium alloy steel member is  $\text{Cr}_2\text{O}_3$ ,



The CO formed in accordance with the formulas (1) to (3) reacts with ammonia as atmosphere gas, and forms HCN in accordance with the following formula (4):

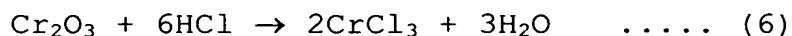


The HCN formed in accordance with the formula (4) reduces the passivated film on the surface of the high-chromium alloy steel member in accordance with the following formula:



The Cs and Ns in the resulting  $\text{Cr}(\text{CN})_3$  diffuse into the surface of the high-chromium alloy steel member, and contribute to carburizing and nitriding so that no residue is formed on the surface of the member.

[0009] The above-described chloride-dependent activation method of a surface of a high-chromium alloy steel member, on the other hand, can be expressed by the following formula (6):



The chromium chloride remains on the surface of the member, and acts as a causative substance for the corrosion

of the member.

Patent Document 1: JP-A-3-44457

Patent Document 2: Japanese Patent Application No. 9-38341

**Problems to be Solved by the Invention**

[0010] As has been described above, the method disclosed in Patent Document 2 is good in that it has theoretically solved the problems of the chloride-dependent activation method for a surface of a metal member as disclosed in Patent Document 1. Nonetheless, the method disclosed in Patent Document 2 is accompanied by a drawback that the use of acetone, which is liquid at normal temperature and pressure, requires facilities for the introduction of acetone vapor and the difficult flow rate control of acetone makes it hard to obtain a metal member having an evenly-activated surface.

[0011] With a view to solving the above-described problems, the present inventors have struggled to develop a method that makes use of a compound, which is gaseous at normal temperature and pressure, in place of acetone involving the problems in handling, leading to the completion of the present invention.

Described specifically, the present invention provides:

1. A method for activating a surface of a metal member, which comprises heating a mixed gas of a carbon donor compound, which is gaseous at normal temperature and pressure, and

ammonia as essential components to at least 300°C in a metal-made heating furnace to form HCN under catalytic action of the metal member, a metal-made inner wall of the furnace or a metal-made jig in the thus-heated mixed gas, and causing the thus-formed HCN to act on the surface of the metal member.

[0012] 2. A method as described above under 1., wherein the carbon donor compound is at least one compound selected from acetylene, ethylene, propane, butane and carbon monoxide.

[0013] 3. A method as described above under 1., wherein the metal-made inner wall of the heating furnace or the metal-made jig contains at least one metal selected from Fe, Ni, Co, Cu, Cr, Mo, Nb, V, Ti and Zr.

[0014] 4. A method as described above under 1., wherein HCN is formed to at least 100 mg/m<sup>3</sup> in the furnace and a furnace atmosphere gas has a dew point not higher than 5°C.

#### **Advantageous Effects of the Invention**

[0015] A passivated film on a surface of a high-alloy steel member makes it difficult to apply diffusion treatment, such as gas nitriding or gas carburizing, that forms a nitrided layer, carburized layer or carbonitrided layer on the surface of the steel member. According to the present invention, an activating treatment method is provided for the surface of the metal member. This method is not accompanied by problems of conventional activation treatment with a halide, such as furnace deposits, furnace wall erosion and effluent

gas detoxification treatment, and is useful as pretreatment for diffusion treatment. According to this method, the passivated surface of the high-alloy steel member can be activated by using a gas commonly employed in gas heat treatment, and forming HCN gas in a heating furnace while making use of catalytic action of the steel member or a surface of the furnace.

#### **Best Modes for Carrying out the Invention**

[0016] The present invention will next be described in more detail based on best modes for carrying out the invention.

According to Patent Document 2 referred to in the above, CH<sub>3</sub>· (methyl radicals) formed by the pyrolysis of acetone in the formula (1) reduce an oxide film on a surface of a metal member. The CO formed in the above-described formula (1) and (2) reacts with ammonia as atmosphere gas on the metal surface to form HCN. HCN acts on the metal oxide film in accordance with the above-described formula (5).

[0017] From a comparison between the formula (2) and the formula (5), the CH<sub>3</sub>· formed by the pyrolysis of acetone and HCN (the reaction product of CO, the other pyrolyzate, with ammonia as atmosphere gas) are similar to each other in their action on the passivated film. The present inventors, therefore, presumed that the existence of both CH<sub>3</sub>· and HCN would be a sufficient condition for the activation of the surface of a high-chromium alloy steel

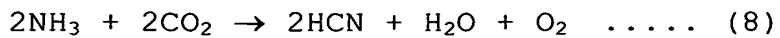
member but would not absolutely be a necessary condition. Paying attention to HCN, the present inventors, therefore, endeavored to develop a method for the formation of HCN on a metal surface and also to ascertain effects of HCN for the activation of the surface of a metal member.

[0018] An investigation was conducted on the formation of HCN by introducing a nitriding atmosphere gas ( $\text{NH}_3:\text{N}_2 = 1:1$  by molar ratio) together with gases selected from various carbon-containing compounds, which are gaseous at normal temperature and pressure, respectively into a Muffle furnace made of SUS310S and heating them to 550°C. As a result, it has been clearly ascertained that carbon monoxide, carbon dioxide, acetylene, ethylene, propane and butane each forms HCN when combined with ammonia.

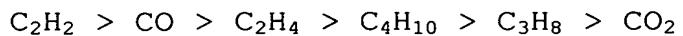
[0019] An experiment was then conducted in a similar manner as described above except that the inner wall of the Muffle furnace was replaced by bricks, and an analysis was performed for the amount of HCN formed. In each case, HCN was not detected. From those results, it has become evident that the catalytic action of a metal surface is an essential condition for the HCN-forming reactions between ammonia and these gases.

[0020] The HCN-forming reactions between ammonia and the above-mentioned carbon-containing compounds can be expressed by the following formulas, respectively:





[0021] To compare the amounts of HCN to be formed by the reactions between the nitriding atmosphere gas ( $\text{NH}_3:\text{N}_2 = 1:1$  by molar ratio) and the gases selected from the various carbon-containing compounds, the reactions of the above-described formulas (7) to (12) were each conducted by incorporating the corresponding carbon-containing compound at 1% in terms of equivalent ratio in the nitriding atmosphere gas ( $\text{NH}_3:\text{N}_2 = 1:1$  by molar ratio), introducing the resultant mixed gas into a Muffle furnace the inner wall of which was made of SUS310S, and then heating the mixed gas at 550°C for 30 minutes. As a result, the amounts of HCN formed from the respective carbon-containing compounds decreased in the following order:



[0022] With respect to these carbon-containing compounds ascertained to form HCN through their reactions with the nitriding atmosphere gas, these compounds were each introduced into a heating furnace at an initial stage of nitriding treatment and then assessed with an SUS304 plate to determine whether or not they have activating effect. As a result, compared with control nitriding treatment

without introduction of any carbon-containing compound,  $C_2H_2$ ,  $CO$ ,  $C_2H_4$ ,  $C_4H_{10}$  and  $C_3H_8$  have been found to be equipped with profound effects on such SUS304 plates in both the evenness of nitriding and the weight increase by the penetration of nitrogen. When  $CO_2$  was used, on the other hand, no difference was observed from the control nitriding treatment in both the evenness of nitriding treatment and the weight increase of the specimen. Concerning  $CO_2$ , no activating effect was, therefore, recognized for the surface of the SUS304 plate.

[0023] The availability of no activating effect for the surface of the SUS304 plate despite the formation of HCN in the furnace by the introduction of  $CO_2$  is presumably attributed to the re-oxidation of the surface of the SUS304 plate under the oxidation action of  $O_2$  and  $H_2O$ , the byproducts of the HCN-forming reaction in the formula (8). Concerning  $CO$ , HCN is formed as mentioned above. This is inconsistent with the phenomenon that stainless steel is not evenly nitrided in a gas softnitriding atmosphere in which ammonia and CO-containing RX gas exist. This inconsistency may be explained by reasons to be described below. It is to be noted that the term "RX gas" means a gas, which is formed by mixing substantially equal chemical equivalents of a hydrocarbon gas (for example, propane gas, butane gas, or natural gas) and air and causing them to decompose in a catalyst layer maintained at 1,000°C, contains  $CO$  and  $H_2(N_2)$  as a primary component and small amounts of  $CO_2$  and  $H_2O$ ,

and is widely used as a nitriding gas.

[0024] The CO contained in NH<sub>3</sub>:RX gas = 1:1 by molar ratio, a typical composition for gas softnitriding, amounts to about 10% in terms of volume percentage. HCN, which is required for the activation of a surface of a metal member, is therefore presumed to exist sufficiently in a gas softnitriding furnace. In an RX gas the dew point of which is not controlled, however, there are a significant amount of H<sub>2</sub>O (around 2 vol.%) and about 0.5 vol.% of CO<sub>2</sub>. It is, therefore, judged that by their oxidizing action, the activated surface of the SUS304 plate is re-oxidized to prevent the penetration of nitrogen into the surface of the plate.

[0025] When CO gas is selected as a carbon donor compound for the activation of a surface of a metal member, it is thus desired to use CO gas singly instead of RX gas. Because the amount of CO gas required to be injected in the present invention is as little as 1/10 (by volume) or so of a gas softnitriding atmosphere, the effects of H<sub>2</sub>O and CO<sub>2</sub> in RX gas are reduced so that RX gas may be used as a CO source in some instances.

[0026] Judging from the formulas on the right-hand sides in the reaction formulas (7) to (12), the byproducts in the case of CO<sub>2</sub> have the highest oxidizing action among these compounds having cyan-forming effect, followed by CO, and the hydrocarbon compounds all form reducing hydrogen. To avoid re-oxidation, it is, therefore, desired to choose a

hydrocarbon compound as a carbon donor compound.

[0027] The activating effect for the surface of the alloy steel member in the present invention is attributed to HCN. The above-described activating effect is dependent on the concentration of HCN in the furnace atmosphere. To obtain satisfactory activating effect, the concentration of HCN can appropriately be in a range of from 100 to 30,000 mg/m<sup>3</sup>. At an HCN concentration lower than 100 mg/m<sup>3</sup>, the above-described activating effect cannot be expected. At an HCN concentration higher than 30,000 mg/m<sup>3</sup>, on the other hand, the above-described activating effect is saturated, resulting not only in an economical disadvantage but also in the occurrence of sooting (the formation of carbon in the furnace) by pyrolysis of the carbon donor compound. Therefore, HCN concentrations outside the above-described range are not preferred.

Further, the dew point of the furnace atmosphere gas may preferably be 5°C or lower. If the dew point is higher than 5°C, the metal surface activated by HCN gas is re-oxidized with H<sub>2</sub>O in the atmosphere and accordingly, is passivated back again.

[0028] The method according to the present invention is also advantageous from the environmental standpoint in that as explained in the reaction formula (5), the HCN attributed to the activation of the surface of the metal member is absorbed into the member and attributes to the nitriding

and carburizing of the member to leave no residue on the surface of the member and the HCN discharged as effluent gas without any contribution to the reaction can be readily burned and detoxified in an ammonia combustion facility arranged as an attachment for the nitriding facility to obviate any new additional facility.

[0029] A further advantage of the present invention is that the time of nitriding treatment can be shortened owing to the smooth progress of the steps in the nitriding treatment process. Gas nitriding of a metal member is generally conducted in such a schedule as will be described below.

[0030] The metal member is set in a furnace, and subsequent to vacuum purging or nitrogen gas replacement of the air in the furnace, the temperature is raised to a nitriding temperature of the metal member and is then maintained constantly at the temperature, both while introducing the nitriding atmosphere gas ( $\text{NH}_3 + \text{N}_2$ ) at a rate as much as 1 to 10 times the internal volume of the furnace per hour. During the treatment, the internal pressure of the furnace is maintained at atmospheric pressure + 0.5 kPa or so by a pressure control valve, and the force-out effluent gas is caused to burn and decompose in an effluent gas combustion facility.

[0031] According to the method disclosed in Patent Document 1 and making use of the fluorine-based gas, it is necessary, subsequent to the introduction of the fluorine-based gas

and the activation treatment of the member, to exhaust the fluorine-based gas and then to introduce the nitriding atmosphere gas into the furnace as disclosed in the examples of the specification of Japanese Patent No. 2,501,925.

[0032] In the present invention, on the other hand, the carbon donor compound is introduced into the nitriding atmosphere gas during the step in which the metal member is heated to the nitriding treatment temperature. As a consequence, HCN is formed to activate the surface of the metal member, and the subsequent termination of the introduction of the carbon donor compound makes it possible to advance directly to the nitriding step. As a result, the treatment time of the nitriding step is substantially shortened, thereby making it possible to fundamentally eliminate the re-oxidation phenomenon of the surface of the metal member which has until now remained as a problem in the conventional treatment upon advancing from the activation step to the nitriding step.

[0033] The present invention has such technical features and advantageous effects as described above. A description will hereinafter be made about certain preferred embodiments of the present invention. In the treatment furnace for use in the present invention, the inner wall can preferably be made of metal. Even if the inner wall is not made of metal, the present invention can still be practiced provided that the metal member to be treated acts as a catalyst for the formation of HCN or a jig adapted to hold the metal member

within the furnace is made of metal. The metal that makes up the metal-made inner wall, metal member or jig may preferably contain, for example, one or more metals selected from Fe, Ni, Co, Cu, Cr, Mo, Nb, V, Ti and Zr.

[0034] Examples of metal members which can be subjected to surface activation treatment by the method of the present invention include members of cold-working die steel, hot-working die steel, plastic die steel, high-speed tool steel, powder metal high-speed tool steel, chrome-molybdenum steel, maraging steel, austenitic stainless steel, ferritic stainless steel, martensitic stainless steel, martensitic heat-resisting steel, austenitic heat-resisting steel or nickel-based superalloys. In the above-described treatment furnace, these metal members are held by suitable jigs and are subjected to surface activation treatment in a manner known *per se* in the art.

[0035] The surface treatment gases to be fed into the furnace are the carbon donor compound, which is gaseous at normal temperature and pressure, and ammonia, which are fed from their own gas cylinders into the furnace. After the metal member is set in the furnace and the internal air of the furnace is purged under vacuum or is replaced with nitrogen gas, the nitriding atmosphere gas (ammonia alone, ammonia + nitrogen gas, or ammonia + nitrogen gas + hydrogen gas) is introduced into the furnace to establish a reducing

atmosphere. Subsequently, heating is initiated, followed by the introduction of the carbon donor compound useful in the present invention. The ammonia gas and carbon donor compound form HCN under the catalytic action of the metal surface when they are heated to 300°C or higher in the furnace. The ratio of the flow rate of ammonia as a nitriding atmosphere gas to that of the introduced carbon donor compound should be controlled within a range of from 1:0.0001 to 1:0.1. If the flow rate of the carbon donor compound is so low that the flow rate ratio becomes smaller than 1:0.0001, HCN is formed too little to bring about its activating effect. If the flow rate of the carbon donor compound is so high that the flow rate ratio becomes greater than 1:0.1, on the other hand, the activating effect is saturated to result in an economical disadvantage.

[0036] The carbon donor compound is composed of one or more gaseous compounds selected from acetylene, ethylene, propane, butane and carbon monoxide as described above, and can be fed into the treatment furnace concurrently with the ammonia-containing gas as mentioned above. It is preferred for the efficient utilization of the carbon donor compound to initiate the introduction of the carbon donor compound at the time point that the temperature of the ammonia-containing gas within the furnace has reached about 300°C. To raise the concentration of the carbon donor compound in the furnace atmosphere at such an early stage

as permitting shortening the treatment time, however, it is desired to introduce the carbon donor compound at the same time as the initiation of heating and to assure the formation of HCN from the initial stage.

### **Examples**

[0037] Based on examples and a comparative example, the present invention will hereinafter be described more specifically. It is to be noted that the following examples and comparative example were conducted using a treatment furnace of the construction illustrated in FIG. 1. FIG. 1 shows a Muffle furnace 1, an outer shell 2 of the Muffle furnace, a heater 3, an internal container (retort) 4, a gas inlet pipe 5, an exhaust pipe 6, a motor 7, a fan 8, a metal-made jig 9, a gas guide cylinder 10, an inverted funnel 11, a vacuum pump 12, an effluent gas combustion facility 13, a carbon donor compound gas cylinder 14, an ammonia gas cylinder 15, a nitrogen gas cylinder 16, a hydrogen gas cylinder 17, a flowratemeter 18, and a gas control valve 19.

[0038] Example 1

Using the SUS310S Muffle furnace of 100-L internal capacity shown in FIG. 1, SUS304 plates were set in the furnace, NH<sub>3</sub> gas and N<sub>2</sub> gas were fed at flow rates of 200 L/H, respectively, and the furnace atmosphere was heated from room temperature to 550°C in 75 minutes. At the time point

that the atmosphere temperature had reached 100°C in the course of the heating (at the 18<sup>th</sup> minute after the initiation of the heating), an injection of acetylene gas was initiated at 2 L/hr. After heated to 550°C, the atmosphere temperature was maintained for 2 hours. At that time point, the injection of acetylene gas was terminated and instead, NH<sub>3</sub> gas and N<sub>2</sub> gas were then fed at 550°C for 4 hours to allow nitriding to proceed. Subsequently, the heating was stopped and N<sub>2</sub> gas alone was continuously fed to cool down the furnace. When the atmosphere temperature had dropped to 100°C or lower, the specimens were taken out of the furnace.

[0039] Effluent gas from the furnace was branched off to have a portion of the effluent gas absorbed in a 2 wt.% aqueous solution of caustic soda, and an analysis was performed for HCN. From the analysis results of the HCN-absorbed solution, the average HCN concentration in the furnace atmosphere during the acetylene gas injection period was 8,000 mg/m<sup>3</sup>. Some of the SUS304 specimens were weighed to determine a weight increase after the nitriding treatment. As a result, the weight increase was determined to be 20 g/m<sup>2</sup>. Some of the SUS304 specimens were cut, and their cut surfaces were polished, etched with Marble's solution, and then observed under an optical microscope. Nitrided layers of 50-μm uniform thickness were found to be formed (a 500× micrograph is shown in FIG. 2). Some of the remaining specimens were measured for surface hardness at 5 points by a Vickers

hardness tester. All the values (H<sub>v</sub>) distributed between 1,200 and 1,250.

[0040] Example 2

SUS304 plates were set in the Muffle furnace employed in Example 1, NH<sub>3</sub> gas and N<sub>2</sub> gas were fed at flow rates of 200 L/H, respectively, and the furnace atmosphere was heated from room temperature to 550°C in 75 minutes. At the time point that the atmosphere temperature had reached 100°C in the course of the heating (at the 18<sup>th</sup> minute after the initiation of the heating), an injection of propane gas was initiated at 5 L/hr. After heated to 550°C, the atmosphere temperature was maintained for 2 hours. At that time point, the injection of propane gas was terminated and instead, NH<sub>3</sub> gas and N<sub>2</sub> gas were then fed at 550°C for 4 hours to allow nitriding to proceed. Subsequently, the heating was stopped and N<sub>2</sub> gas alone was continuously fed to cool down the furnace. When the atmosphere temperature had dropped to 100°C or lower, the specimens were taken out of the furnace.

[0041] Effluent gas from the furnace was branched off to have a portion of the effluent gas absorbed in a 2 wt.% aqueous solution of caustic soda, and an analysis was performed for HCN. From the analysis results of the HCN-absorbed solution, the average HCN concentration in the furnace atmosphere during the propane gas injection period was 400 mg/m<sup>3</sup>. Some of the SUS304 specimens were weighed to determine a weight increase after the nitriding treatment. As a result, the

weight increase was determined to be 18 g/m<sup>2</sup>. Some of the SUS304 specimens were cut, and their cut surfaces were polished, etched with Marble's solution, and then observed under an optical microscope. Nitrided layers of 45-μm uniform thickness were found to be formed. Some of the remaining specimens were measured for surface hardness at 5 points by a Vickers hardness tester. All the values (Hv) distributed between 1,200 and 1,250.

[0042] Example 3

SUS304 plates were set in the Muffle furnace employed in Example 1, NH<sub>3</sub> gas and N<sub>2</sub> gas were fed at flow rates of 200 L/H, respectively, and the furnace atmosphere was heated from room temperature to 550°C in 75 minutes. At the time point that the atmosphere temperature had reached 100°C in the course of the heating (at the 18<sup>th</sup> minute after the initiation of the heating), an injection of CO gas was initiated at 5 L/hr. After heated to 550°C, the atmosphere temperature was maintained for 2 hours. At that time point, the injection of CO gas was terminated and instead, NH<sub>3</sub> gas and N<sub>2</sub> gas were then fed for 4 hours to allow nitriding to proceed. Subsequently, the heating was stopped and N<sub>2</sub> gas alone was continuously fed at 550°C to cool down the furnace. When the atmosphere temperature had dropped to 100°C or lower, the specimens were taken out of the furnace.

[0043] Effluent gas from the furnace was branched off to have a portion of the effluent gas absorbed in a 2 wt.% aqueous

solution of caustic soda, and an analysis was performed for HCN. From the analysis results of the HCN-absorbed solution, the average HCN concentration in the furnace atmosphere during the CO gas injection period was 1,000 mg/m<sup>3</sup>. Some of the SUS304 specimens were weighed to determine a weight increase after the nitriding treatment. As a result, the weight increase was determined to be 18 g/m<sup>2</sup>. Some of the SUS304 specimens were cut, and their cut surfaces were polished, etched with Marble's solution, and then observed under an optical microscope. Nitrided layers of 45-μm uniform thickness were found to be formed. Some of the remaining specimens were measured for surface hardness at 5 points by a Vickers hardness tester. All the values (Hv) distributed between 1,200 and 1,250.

[0044] Example 4

SUS304 plates were set in the Muffle furnace employed in Example 1, NH<sub>3</sub> gas and N<sub>2</sub> gas were fed at flow rates of 200 L/H, respectively, and the furnace atmosphere was heated from room temperature to 550°C in 75 minutes. At the time point that the atmosphere temperature had reached 100°C in the course of the heating (at the 18<sup>th</sup> minute after the initiation of the heating), an injection of C<sub>2</sub>H<sub>4</sub> gas was initiated at 5 L/hr. After heated to 550°C, the atmosphere temperature was maintained for 2 hours. At that time point, the injection of C<sub>2</sub>H<sub>4</sub> gas was terminated and instead, NH<sub>3</sub> gas and N<sub>2</sub> gas were then fed at 550°C for 4 hours to allow

nitriding to proceed. Subsequently, the heating was stopped and N<sub>2</sub> gas alone was continuously fed to cool down the furnace. When the atmosphere temperature had dropped to 100°C or lower, the specimens were taken out of the furnace.

[0045] Effluent gas from the furnace was branched off to have a portion of the effluent gas absorbed in a 2 wt.% aqueous solution of caustic soda, and an analysis was performed for HCN. From the analysis results of the HCN-absorbed solution, the average HCN concentration in the furnace atmosphere during the C<sub>2</sub>H<sub>4</sub> gas injection period was 1,200 mg/m<sup>3</sup>. Some of the SUS304 specimens were weighed to determine a weight increase after the nitriding treatment. As a result, the weight increase was determined to be 18 g/m<sup>2</sup>. Some of the SUS304 specimens were cut, and their cut surfaces were polished, etched with Marble's solution, and then observed under an optical microscope. Nitrided layers of 45-μm uniform thickness were found to be formed. Some of the remaining specimens were measured for surface hardness at 5 points by a Vickers hardness tester. All the values (Hv) distributed between 1,200 and 1,250.

[0046] Example 5

SUS304 plates were set in the Muffle furnace employed in Example 1, NH<sub>3</sub> gas and N<sub>2</sub> gas were fed at flow rates of 200 L/H, respectively, and the furnace atmosphere was heated from room temperature to 550°C in 75 minutes. At the time point that the atmosphere temperature had reached 100°C in

the course of the heating (at the 18<sup>th</sup> minute after the initiation of the heating), an injection of C<sub>4</sub>H<sub>10</sub> gas was initiated at 5 L/hr. After heated to 550°C, the atmosphere temperature was maintained for 2 hours. At that time point, the injection of C<sub>4</sub>H<sub>10</sub> gas was terminated and instead, NH<sub>3</sub> gas and N<sub>2</sub> gas were then fed at 550°C for 4 hours to allow nitriding to proceed. Subsequently, the heating was stopped and N<sub>2</sub> gas alone was continuously fed to cool down the furnace. When the atmosphere temperature had dropped to 100°C or lower, the specimens were taken out of the furnace.

[0047] Effluent gas from the furnace was branched off to have a portion of the effluent gas absorbed in a 2 wt.% aqueous solution of caustic soda, and an analysis was performed for HCN. From the analysis results of the HCN-absorbed solution, the average HCN concentration in the furnace atmosphere during the C<sub>4</sub>H<sub>10</sub> gas injection period was 600 mg/m<sup>3</sup>. Some of the SUS304 specimens were weighed to determine a weight increase after the nitriding treatment. As a result, the weight increase was determined to be 18 g/m<sup>2</sup>. Some of the SUS304 specimens were cut, and their cut surfaces were polished, etched with Marble's solution, and then observed under an optical microscope. Nitrided layers of 45-μm uniform thickness were found to be formed. Some of the remaining specimens were measured for surface hardness at 5 points by a Vickers hardness tester. All the values (Hv) distributed between 1,200 and 1,250.

## [0048] Comparative Example 1

SUS304 plates were set in the Muffle furnace employed in Example 1, NH<sub>3</sub> gas and N<sub>2</sub> gas were fed at flow rates of 200 L/H, respectively, and the furnace atmosphere was heated from room temperature to 550°C in 75 minutes. After heated to 550°C, the atmosphere temperature was maintained for 6 hours. NH<sub>3</sub> gas and N<sub>2</sub> gas were continuously fed to allow nitriding to proceed. Subsequently, the heating was stopped and N<sub>2</sub> gas alone was continuously fed to cool down the furnace. When the atmosphere temperature had dropped to 100°C or lower, the specimens were taken out of the furnace.

[0049] Effluent gas from the furnace was branched off to have a portion of the effluent gas absorbed in a 2 wt.% aqueous solution of caustic soda, and an analysis was performed for HCN. From the analysis results of the HCN-absorbed solution, HCN was not detected at all, thereby ascertaining that HCN did not exist at all in the furnace atmosphere. Some of the SUS304 specimens were weighed to determine a weight increase after the nitriding treatment. As a result, the weight increase was determined to be 10 g/m<sup>2</sup>. Some of the SUS304 specimens were cut, and their cut surfaces were polished, etched with Marble's solution, and then observed under an optical microscope. Nitrided layers of uneven thicknesses of from 8 to 18 μm were found to be formed (a 500× micrograph is shown in FIG. 3). Some of the remaining specimens were measured for surface hardness at 5 points

by a Vickers hardness tester. The values (Hv) considerably varied from 500 to 1,100, and their absolute values were found to be lower compared with the corresponding values of the examples.

### **Industrial Applicability**

[0050] A passivated film on a surface of a high-alloy steel member makes it difficult to apply diffusion treatment, such as gas nitriding or gas carburizing, that forms a nitrided layer, carburized layer or carbonitrided layer on the surface of the steel member. According to the present invention, an activating treatment method is provided for the surface of the metal member. This method is not accompanied by problems of conventional activation treatment with a halide, such as furnace deposits, furnace wall erosion and effluent gas detoxification treatment, and is useful as pretreatment for diffusion treatment. According to this method, the passivated surface of the high-alloy steel member can be activated by using a gas commonly employed in gas heat treatment, and forming HCN gas in a heating furnace while making use of catalytic action of the steel member or a surface of the furnace.

### **Brief Description of the Drawings**

[0051] [FIG. 1] A diagram illustrating the construction of a treatment furnace useful in the present invention.

[FIG. 2] A micrograph of a cut surface of a specimen of Example 1.

[FIG. 3] A micrograph of a cut surface of a specimen of Comparative Example 1.

[0052] 1: Muffle furnace  
2: Outer  
3: Heater  
4: Internal container (retort)  
5: Gas inlet pipe  
6: Exhaust pipe  
7: Motor  
8: Fan  
9: Metal-made jig  
10: Gas guide cylinder  
11: Inverted funnel  
12: Vacuum pump  
13: Effluent gas combustion facility  
14: Carbon donor compound gas cylinder  
15: Ammonia gas cylinder  
16: Nitrogen gas cylinder  
17: Hydrogen gas cylinder  
18: Flowratemeter  
19: Gas control valve